KINETICS OF MICRODOMAIN FORMATION IN TWO DIMENSIONAL ASSEMBLIES *

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A novel phenomenological approach to the microdomain structure formation or phase transformation in two-dimensional cooperative systems is proposed. The theory offered states that a new structure consists of pieces of islands, microdomains, germs, *etc.* and deals with modeling of the pattern formation process with increase of area of a new structure or phase. The kinetics of the process is studied. Probabilistic characteristics are obtained and first three moments of the process are analyzed.

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1. Introduction

Interest in kinetics and spatio-temporal behavior of microstructure formation of a cooperative and possibly multicomponent system like metallic films, nonmetallic (ceramics or polymers) membranes or even organic ultra-thin films (biomembranes) is of permanent interest to material scientists, physicists, and chemists but recently also attracts interest of technologists or processing engineers [1]. Among many types of growth and structure formation processes (see, *e.g.* [2] for going into details) the normal grain growth, first related to metallic and ceramic of two- and three-dimensional materials [3–6], may serve as a properly chosen setting for the microdomain formation in which both a quite large complexity of the cluster population in systems as well as a certain competition within it are constantly present [7]. Up to now, this phenomenon has mostly been modeled using the Monte Carlo technique (*cf.* [4, 6]) and by exploring a statistical description based on diffusion-type equations for evolution of the grain population when fluctuations of the grain boundary are imposed on the system. It has been possible to find some other descriptions of this process, *e.g.* the mechanism of reduction of the grain boundary energy or a very recent geometric approach based on the Voronoi mosaic concept [5, 6, 8]. Because the systems studied are generically interaction systems in which grains (microdomains) constantly change surface atoms or molecules, it seems to be quite reasonable to assume that such a type of theoretical description could also be offered for explaining some more complicated physical situations. *E.g.,* we think of the processes that quite naturally may occur in two-dimensional materials (films, membranes, coatings, layers) understood here as physical assemblies made of smaller subunits.

In this work, we wish to consider the structure formation or phase transformation processes accompanied by increase of domain of a new structure or phase [9]. This increase means that, contrary to the normal grain growth [3, 10, 11] of materials, the first moment representing the whole area of a new phase is an increasing function of time. The zero-moment, equivalent to a number of domains comprising the assembly, is calculated and exhibits similar asymptotics as that known from the normal grain growth process in two dimensions [5, 6]. Our treatment can also be understood as a kind of multi-compartment analysis [12] applied quite often for the description of some physical situations in which there exists a system composed of compartments (here grains or microdomains) separated by interfaces and among which permanent exchange of matter takes place.

In Section 2, a presentation of the model is given. The process is described by a diffusion-type equation with imposed boundary and initial conditions. The solution of the equation is given in the Section 2. In Section 3,

analysis of first three moments is carried out. The Section 4 serves for final conclusions.

2. Presentation of the model and its solution

Let us begin our considerations by stating that there are a few basic theories of the normal grain growth with different kind of mechanisms driving the growth, *i.e.* caused by the surface tension of the curved boundaries or caused by random fluctuations of the grain boundaries. The last is called the random walk model [4–6]. In this case, the mechanism for the growth of a new phase is the migration of particles across the boundaries. Individual particles or clusters of atoms move from one grains to their neighbours or particles of an old phase (surroundings) attach to grains changing their area. In consequence, grains grow by gaining or losing atoms and if any grain shrinks to zero size then it cannot re-nucleate and is lost for ever. The second mechanism is properly constructed when the grain boundary energy is negligible in comparison to the thermal energy of the boundary atoms and this is the case when the thermal fluctuations are important for the growth kinetics. In this case, the driving force for growth is the decrease of the total grain boundary energy only [13]. In the theory proposed we look for the more physical modification of the normal grain growth which includes some effects of increase of total area of all grains and also reproduces fairly well some known physical characteristics of the process. Here we have in mind *e.g.* some metallurgical systems in which during the anealing or recrystallization process some possible enlargement of material area (volume, for three-dimensional system) can take place (*cf.* [3, 11] and references therein). In our modeling we assume that the spatio-temporal evolution of the system to a new phase is represented by the continuity equation

$$\frac{\partial}{\partial t} f(s,t) = -\frac{\partial}{\partial s} J(s,t)\,, \quad s \in [0,\infty]\,, \tag{1}$$

where $f(s,t)$ is the distribution function of microdomains of a new phase of area (volume) s at time t, *i.e.*, $f(s,t)ds$ is a number of domains (islands, clusters) of area (volume) s. The particle flux $J(s,t)$ is of the Fick form

$$J(s,t) = -D(s)\frac{\partial}{\partial s} f(s,t)\,. \tag{2}$$

A form of the function $D(s)$ depends on dimension of the system and is given by

$$D(s) \sim s^{\alpha}\,. \tag{3}$$

It should be related to the net flux of the migrating particles through the domain boundaries which for two-dimensional systems is proportional to the length of the boundary (circumference) of domains [6], that is,

$$D(s) \sim s^{1/2} \quad \text{and} \quad \alpha = \tfrac{1}{2}. \tag{4}$$

This relation represents the scaling law of the number of available surface sites (particles) with grain area [14]. For Eq. (1), two boundary conditions have to be prescribed at the endpoints of the interval $[0, \infty]$. These are the Dirichlet boundary conditions [6],

$$f(0,t) = f(\infty,t) = 0. \tag{5}$$

They mean that the number of domains of zero and of infinite area at any instant t is zero. Eq. (1)–(3) resembles an equation for diffusion processes. However, in the case considered it is not a diffusion process. In particular, normalization of $f(s,t)$ does not hold. To solve the parabolic partial differential equations (1)–(2) with the "diffusion function" (3), let us introduce the function $\mathcal{F}_\lambda(s)$ of two variables λ and s by the relation

$$f(s,t) = \int_0^\infty \mathrm{e}^{-\lambda t}\mathcal{F}_\lambda(s)d\lambda. \tag{6}$$

Then from (1)–(3) it follows that $\mathcal{F}_\lambda(s)$ obeys an ordinary differential equation of the second order of the form

$$s^\alpha \mathcal{F}''_\lambda(s) + \alpha s^{\alpha-1}\mathcal{F}'_\lambda(s) + \lambda\mathcal{F}_\lambda(s) = 0, \tag{7}$$

where the prime denotes a derivative with respect to s. For a two dimensional systems, when $\alpha = 1/2$ and Eq. (4) holds, then Eq. (7) reduces to the form

$$2s\mathcal{F}''_\lambda(s) + \mathcal{F}'_\lambda(s) + 2\lambda\sqrt{s}\mathcal{F}_\lambda(s) = 0. \tag{8}$$

Introducing the new variable

$$y = \sqrt{s} \tag{9}$$

and defining the function $F_\lambda(y)$ by the relation

$$F_\lambda(y) = \mathcal{F}_\lambda(s) \tag{10}$$

convert (8) into the equation

$$F''_\lambda(y) + 4\lambda y F_\lambda(y) = 0. \tag{11}$$

A general solution of this equation reads (take into account the equalities (9) and (10)) [15]

$$F_\lambda(y) = \mathcal{F}_\lambda(s) = s^{1/4}\left[C_1(\lambda)J_{1/3}\left(\frac{4}{3}\sqrt{\lambda}s^{3/4}\right) + C_2(\lambda)J_{-1/3}\left(\frac{4}{3}\sqrt{\lambda}s^{3/4}\right)\right] \quad (12)$$

with two "constants" $C_1(\lambda)$ and $C_2(\lambda)$ and $J_\nu(x)$ being a Bessel function [16]. The function $J_{-1/3}\left(4\sqrt{\lambda}s^{3/4}/3\right)$ diverges as $s^{-1/4}$ for $s \to 0$. Therefore in order to fulfil the boundary conditions (5) for (12), one should put $C_2(\lambda) = 0$. Hence, from (6) and (12) one gets

$$f(s,t) = 2s^{1/4}\int_0^\infty dzze^{-tz^2}B(z)J_{1/3}\left(\frac{4}{3}zs^{3/4}\right), \quad (13)$$

where the new integration variable $z = \sqrt{\lambda}$ has been introduced and $B(z) = C_1(z^2)$ is a function determined by an initial distribution $f(s,0)$. When $t \to 0$ then (13) becomes

$$f(s,0) = 2s^{1/4}\int_0^\infty dzzB(z)J_{1/3}\left(\frac{4}{3}zs^{3/4}\right). \quad (14)$$

Applying the theory of Bessel transforms [17], one can solve this integral equation with respect to unknown function $B(z)$ and then $B(z)$ is expressed as an integral functional of $f(s,0)$. *E.g.*, let us assume that initially at $t = 0$ there are N_0 microdomains of area s_0. It corresponds to the initial condition

$$f(s,0) = N_0\delta(s - s_0), \quad (15)$$

where $\delta(x)$ is a Dirac delta distribution. In this case

$$B(z) = AJ_{1/3}\left(\frac{4}{3}zs_0^{3/4}\right), \quad (16)$$

where

$$A = \frac{2}{3}s_0^{1/4}N_0. \quad (17)$$

Substituting (16) into (13) and integrating over z [18], one finally gets the solution of the problem (1)–(2) and (4) in the following explicit form

$$f(s,t) = \frac{A}{t}\exp\left(-\frac{b^2}{4t}\right)s^{1/4}\exp\left(-\frac{4}{9t}\left(s^{3/4}\right)^2\right)I_{1/3}\left(\frac{2b}{3t}s^{3/4}\right), \quad (18)$$

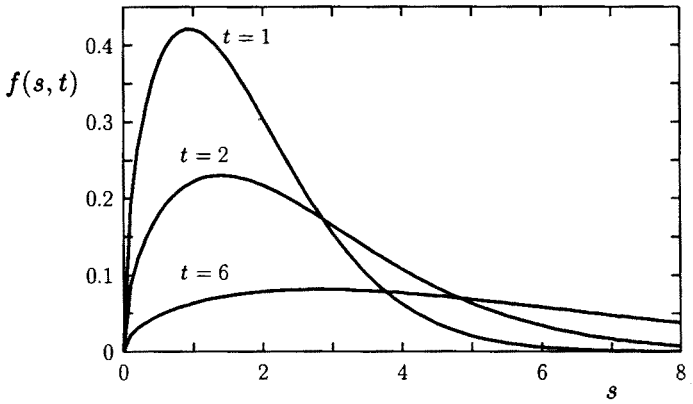

Fig. 1. Dependence of the distribution function $f(s,t)$ on area s of the microdomains for three instants (values of parameters $A = 1$ and $b = 1$).

where $I_\nu(x)$ is a modified Bessel function [16] and

$$b = \frac{4}{3} s_0^{3/4}. \tag{19}$$

The function (18) is visualized in Fig. 1 for three different time instants. Starting from the initial Dirac delta distribution (15), concentrated about the initial area $s = s_0$ of microdomains, maximum of $f(s,t)$ is smaller and smaller, and is shifted from smaller to greater values of area when time increases. It means that microdomains grow in time. Other characteristics of the process are analyzed in the next section.

3. Time-characteristics of the process

The distribution $f(s,t)$ allows to evaluate the basic characteristics of the process like moments

$$\langle s^n(t) \rangle = \int_0^\infty s^n f(s,t) ds, \quad n = 0, 1, 2, \ldots \tag{20}$$

of the process. The zero-moment, $\langle s^0(t) \rangle$, is equal to the number of microdomains in the system and is expressed as [18]

$$\langle s^0(t) \rangle = A \frac{3^{2/3}}{2^{1/3} \Gamma(1/3)} b^{-1/3} \gamma\left(\frac{1}{3}, \frac{b^2}{4t}\right), \tag{21}$$

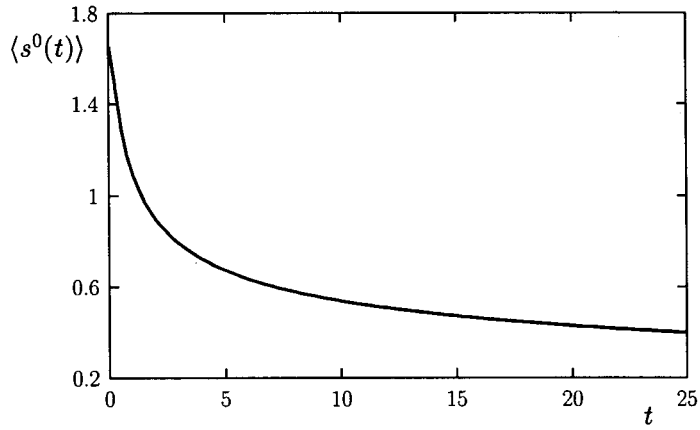

Fig. 2. The number of microdomains (the zero-moment of the process) is shown versus time ($A = 1$ and $b = 1$).

where $\gamma(\alpha, x)$ stands for a reduced gamma function and $\Gamma(x)$ is an Euler gamma function [16]. Since $\gamma(\alpha, x)$ is an increasing function of x, it means that the number of microdomains in the system decreases with increasing time (*cf.* Fig. 2).
For long times, it decays powerly in time as

$$\langle s^0(t)\rangle \sim t^{-1/3}, \qquad t \gg 1\,. \tag{22}$$

The first moment, $\langle s^1(t)\rangle$, is a total area S of all microdomains and is given by the relation [18]

$$\begin{aligned} S &= \langle s^1(t)\rangle \\ &= A\frac{9}{2^{4/3}}\frac{\Gamma(2/3)}{\Gamma(1/3)}b^{1/3}t^{1/3}\exp\left(-\frac{b^2}{4t}\right){}_1F_1\left(\frac{5}{3};\frac{4}{3};\frac{b^2}{4t}\right), \end{aligned} \tag{23}$$

where ${}_1F_1(\alpha;\beta;z)$ is a Kummer (confluent hypergeometric) function [16]. On the contrary, the total area of all domains grows in time (see Fig. 3). Its long-time asymptotics displays the power-law time dependence,

$$S \sim t^{1/3}, \qquad t \gg 1\,. \tag{24}$$

In turn, the second moment, $\langle s^2(t)\rangle$, increases linearly with increasing time [18],

$$\langle s^2(t)\rangle = at + k\,, \tag{25}$$

where a and k are constants,

$$a = A\left(\frac{3^7}{2^5}\right)^{1/3} b^{1/3} \quad \text{and} \quad k = A\left(\frac{3^{10}}{2^{17}}\right)^{1/3} b^{7/3}. \tag{26}$$

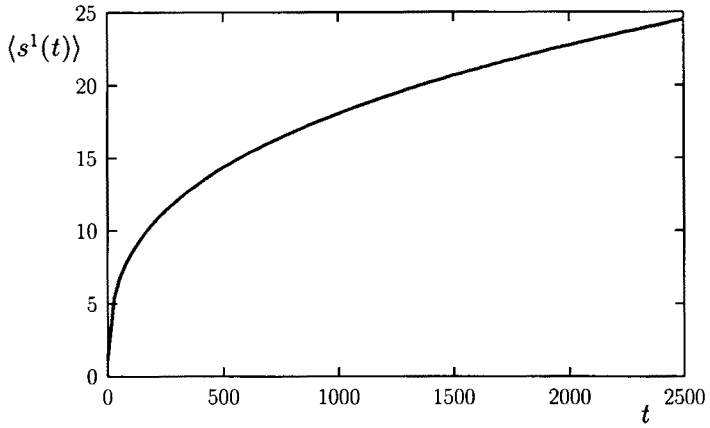

Fig. 3. The total area S of all microdomains (the first-moment of the process) is presented as a function of time (for $A = 1$ and $b = 1$).

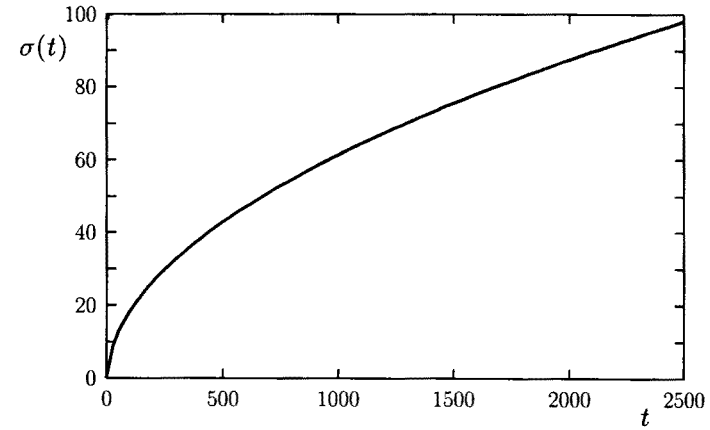

Fig. 4. Time-evolution of fluctuations $\sigma(t) = \sqrt{\langle s^2(t)\rangle - \langle s^1(t)\rangle^2}$ of the process ($A = 1$ and $b = 1$).

From Eqs (23) and (25) it follows that fluctuations $\sigma(t)$,

$$\sigma^2(t) = \langle s^2(t)\rangle - \langle s^1(t)\rangle^2, \tag{27}$$

of area of microdomains grows in time (it is presented in Fig. 4). The contribution to the long-time asymptotics of fluctuations comes dominantly from the first term in (25) and behaves as

$$\sigma(t) \sim t^{1/2}, \qquad t \gg 1. \tag{28}$$

One may also conclude on long-time asymptotics of the average radius $r_{\mathrm{av}}(t)$ of the microdomains which is determined from the relation

$$S \propto \langle s^0(t)\rangle r_{\mathrm{av}}^2(t). \tag{29}$$

Taking into account (22) and (24), one can infer that $r_{\mathrm{av}}(t)$ has the Lifshitz–-Slyozov asymptotics [10, 11]

$$r_{\mathrm{av}}(t) \sim t^{1/3}. \tag{30}$$

Note that the case stated above differs distinctly from the "conventional" case $r_{\mathrm{av}}(t) \propto t^{1/2}$ and which is also valid for one-dimensional systems because then the normal grain growth process as well as our model are represented by the standard diffusion equation with a constant diffusion function (*cf.* , [3, 19] for details).

4. Summary

In Section 2 we have presented the description of the growth kinetics of microdomains (grains) in two-dimensional assemblies. It is based on the diffusion-type parabolic equation of the Fickian form with the diffusion coefficient $D(s)$ being a power function of the state s. It is related to the assumption that grains of a new phase grow by attaching new particles, clusters and other grains to the boundary of grains. As a result, a number of grains decreases in time and total area of all grains grows with increasing time. The basic extension of our model relies on the modification of the kinetic equation given by Eqs (1)–(3) and it "impinges" some physical scenario different when comparing with the classical grain growth concept [3, 4, 13]. It has some interesting consequences (*cf.* Section 3), which lead to broader as well as more accurate description of many types of phase transformation and structure formation phenomena not necessary being limited to ceramics or metallic materials. Experimental examples concerning the growth and pattern formation processes are reported elsewhere (*cf.* [1] and references therein). Looking at the results revealed in Section 3, it is clear that the formalism proposed can be applied for the description of the materials which undergo the grain growth conditions but with an increase of area effect that appears during the whole process (the first moment is time-dependent). It is also hopeful that the formalism proposed can serve to elucidate a temporal behavior of biomaterials [20] and biosystems [21]. *E.g.,* in self-aggregation in an insect population, the aggregation process appears to result from the competition between two factors: the random moves of the larvae, and their reaction to a chemical product, a "pheromon" they synthetize from terpenes contained in the tree on which they feed and that each of them emits at a rate depending on its nutrition state. The pheromon diffuses in space, and the larvae move in the direction of its concentration gradient. Such a reaction provides an autocatalytic mechanism since, as they gather in a cluster,

the larvae contribute to enhance the attractiveness of the corresponding region. The higher the local density of larvae in this region, the stronger the gradient and the more intense the tendency to move toward the crowded point. One can observe an analogy with our model.

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